Wetherill C. M.,

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ON THE CRYSTALLINE NATURE OF GLASS.

Presented by J. J. Woodward

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On the Crystalline Nature of Glass.

By Charles M. Wetherill, Ph.D., M.D.[1]

The usual explanation given for the different appearance of etchings by hydrofluoric acid in the gaseous and in the liquid state, is that by employing gas, the products of decomposition of the glass remain in the corroded cavities communicating a ground-glass appearance. This does not obtain by the use of the liquid acid, since in this case the said products are removed from the cavities.

An examination of this subject by the aid of the microscope at once showed that the ordinary explanation is erroneous. Ground glass is seen, under the microscope, to be covered with irregular cavities of uniform size, which act by the dispersion of light to produce the characteristic appearance of glass in this condition.

When glass is exposed to the vapor of hydrofluoric acid, the corrodent is deposited in the condition of minute globules, each of which attacks the surface to which it is attached. Articles of glass placed near the apparatus in which the gas is generated are thus coated with a delicate film of the vapor, and are etched, so that the microscope exhibits extremely minute and shallow cavities in which, after cleansing the surface by water, no trace of other substance than glass is perceptible. When the exposure to the acid fumes is more prolonged, the cavities are deeper and more irregular. A still greater irregularity is effected by a more lengthened action of the corrosive vapor; the acid acts more intensely upon the spots first attacked, and the holes are extended with ragged margins and deepened by the action.

On the other hand, when the glass is immersed in *liquid* hydrofluoric acid, or if a drop of the same be suffered to fall upon the plate, the whole surface is corroded with a certain degree of uniformity. There are no minute points of action as in the case of the deposition of spherules of the acid vapor.

Hydrofluoric acid gas, so called, is thus shown to be a *vapor*, constituted of minute drops, like cloud. It would be interesting to test the effect upon glass of the perfectly anhydrous gas obtained lately. From these considerations, hydrofluoric gas appears to possess in an eminent degree the cloud-forming property of antozone. An appreciable quantity of this substance exists in the Woelsendorf fluor spar, and it may be questioned whether all specimens of this mineral do not contain traces of antozone.

In observing the specimens etched by the liquid acid, the crystalline nature of glass was discovered and witnessed in every

[1] The observations of which an account is here given were made in the laboratory of the Smithsonian Institute, Washington.

case. By an examination of the literature of the subject it was ascertained that Leydolt (Wiener Acad. Bericht, viii, 261) had made this interesting and important discovery. I have been inclined to publish my results because Leydolt's observations do not appear to have received the attention which they merit; because my manner of applying the acid is different; and because crystals were observed of form differing from those described in Leydolt's paper.

In addition to these reasons, his discovery may appear to need a certain confirmation, since Daubrée has asserted (Comptes Rend., xlv, 792) that the crystalline phenomena are due not to the glass, but to the deposition of crystals of fluosilicid of potassium, &c., which retard the corrosive action by protecting the glass under them. In the following experiments with as prolonged a microscopic observation as the object-glass could be trusted to the corrosive fumes, the result of the reaction of a drop of the acid upon the glass appeared to be amorphous. In an experiment in which a watch glass was exposed, with the convex surface downward, as a cover to a platinum crucible containing hydrofluoric acid, a lapse of twelve hours effected a deep corrosion. This was most extensive at the lowest point of the glass where a large drop of liquid was adhering. The solid products of the reaction had settled to the inferior portion of the drop, and some of them had fallen with previous drops into the crucible. A microscopic examination of the glass demonstrated the presence of etched crystals, which could not, under the circumstances, have resulted from a protecting effect of crystals of fluosilicid.

Frankenheim (Jr. pr. Ch., liv, 430) maintains that solid bodies generated from a liquid are always crystalline, although the crystals may be too minute to be perceptible by our present instruments. His arguments, in the cases of glass, resins and the like, are *a priori*, being based upon the analogies proceeding from a study of the general properties of matter. They render the crystalline character of glass very probable.

This chemist places the glasses, resins, and fats in the same category in their relations to crystallization. In the transition of these bodies to liquids by an elevation of temperature, they pass through conditions of softness and semi-fluidity before melting. This softening does not depend upon a malleability, as in the case of metals. Glass, for example, remains perfectly brittle to a certain temperature, and when fusion begins to take place the angles are rounded by the cohesion of the liquid portions and the adhesion of these to the parts not yet melted. At a higher temperature, the liquid portion constitutes the mass of the body, but in it are suspended innumerable solid particles, which communicate to it a sticky or gelatinous character.

When melted glass cools, its least fusible compounds separate at first, and when the refrigeration is gradual a distinct crystallization takes place. By a rapid cooling the crystals must be more numerous and much smaller. If they cannot be detected in such glass by the eye or by aid of the microscope, the reason may be in their extreme tenuity, so that the light behaves to them as to the natural roughness of the polished surface. The author observes that silica is often separated in so fine a condition that it passes through the small pores of the filter. He finds no reason in the phenomena of this class of bodies for an actual amorphism; but assumes that they are composed of *crystals*, which, although really small, are large in relation to the atomic molecules of the bodies.

He concludes (op. cit., p. 476) that "amorphous bodies, in the ordinary sense of the expression, are unknown among solids, for solidity depends upon crystallization."

Gaudin, in his *brochure* (*Reforme de la Chemie Minerale et Organique*, Paris, 1863), endeavors to show what crystalline forms are probable for all bodies, deducing his results from the number of atoms in their chemical formulæ and the simplest manner in which they may be arranged. Chemists are divided as to the reliance to be placed upon Gaudin's views; but if they are tenable, or if in any degree founded upon reasonable grounds, the crystalline condition of all solid bodies would seem to be a necessary consequence.

Pelouze (Comptes Rendus, xl, 1321), in an investigation of the devitrefication of glass, as in the so-called porcelain of Réaumur, exposed a tablet of plate glass to incipient fusion upon the sole of a glass furnace for a period of 24–48 hours, and then suffered it to cool slowly. The result was a porcelain-like substance consisting of numerous opaque acicular crystals which were arranged in parallel series, the individuals being perpendicular to the surface of the plate. It was found that the crystallization proceeded from the surface to the interior of the tablet, and that when the process was arrested there was a distinct line of demarcation between the crystalline and vitreous portions. In rare instances the fibrous structure was wanting, and the crystallization was of such nature that the fractured glass presented the appearance of fine white marble. Occasionally the crystals were replaced by an enamel-like material. In repeated experiments of this character Pelouze found that the glass experienced no change of weight during the devitrefication, and the altered glass was restored to its transparency by a simple fusion. The process might be repeated several times without any alteration of weight. Devitrefied window glass, and more especially bottle glass when in large masses in the melting pots, sometimes exhibited yellowish-green *needles*, which were occasionally *small* and

short, but often exceeded a centimeter in length, being closely adherent one to another and *interwoven in all directions*. The vacant spaces between the crystals recalled the crystallization of sulphur.

The crystallization of the glass was assisted by the addition of infusible or difficultly fusible substances to it when in the pasty condition. This is shown by the following experiment performed upon portions of material weighing one hundred kilograms.

Two melting pots were half filled with the same kind of glass, which was at first melted and then suffered to cool until it had assumed a pasty or tenacious consistence. To one crucible a small quantity of vitreous matter was added, and both pots were suffered to cool. That to which nothing had been added contained a transparent glassy mass, while the material in the other crucible was nearly opaque from crystal aggregations. One per cent of sand added to the pasty glass produced the same effect; and when quartz was employed the mineral retained its transparency, remaining mingled with the devitrefied mass.

Pelouze found that mirror, plate, lead, bottle, and Bohemian glasses were all susceptible of devitrefication, although with different degrees of readiness, the tri-silicate of soda being the most ready. A glass of silica, boracic acid, potassa and zinc yielded mere traces of crystallization; but the combination of silica and boracic acid with potassa and lime could not be devitrefied by an exposure of ninety-six hours to a temperature at which softening took place.

This chemist infers that the change experienced by glass during this process is a physical, and not a chemical one. He states, as the result of many analyses performed by himself, that the crystals do not differ in composition from the vitreous mass in which they are embedded.

Dumas (op. cit.) takes exceptions to some of Pelouze's inferences, having found a difference in the constitution of the glassy and crystallized portions of the mass. Thus, in respect to silica; for the vitreous portion 64·7 per cent, and in the crystals 68·2.

Leblanc found in the two kinds respectively: for mirror glass 66·2 and 69·3; for bottle glass 57·9 and 62·95. In the bottle glass Leblanc found that the transparent portions contained 1·57 per cent of protoxyd of iron, although only indistinct traces of this base were detected in the opaque part.

Dumas therefore holds that the products obtained by Pelouze are "analogous to *mixtures of the fatty acids*, which by fusion form a homogeneous liquid, which by cooling gives a fibrous solid, in which although the eye can perceive nothing heterogeneous, each acid has separated in its own crystal form."

Terreil (Comptes Rendus, xlv, 693) observed in the melting pots of a glass furnace which had cooled very slowly, a perfectly

crystalline mass which contained cavities with small transparent crystals. These had a composition similar to that of a transparent bottle glass prepared from the same materials in the same proportions. Thus:

	Glass crystals.	Bottle glass.
Silica,	55·85	56·84
Lime,	24·14	21·15
Magnesia,	7·63	6·37
Alumina,	2·22	3·64
Peroxyd iron,	1·06	2·59
Soda,	8·47	8·69
Potassa,	0·63	0·40
Manganese,	traces	traces
	100·00	99·68
Spec. gravity,	2·824	2·724

For the composition of a partially devitrefied glass which was formed in the same furnace, under different circumstances, he found:

	Vitreous part.	Devitrefied part.
Silica,	62·40	63·67
Lime,	18·14	18·65
Magnesia,	4·47	6·12
Alumina,	7·21	4·98
Peroxyd iron,	2·66	0·71
Alkalies,	5·12	5·87
Manganese,	traces	traces
	100·00	100·00
Spec. gravity,	2·610	2·857

Leydolt (Wien. Acad. Bericht, viii, 261) introduces his experiments upon glass etching by observations of himself and others upon specimens of glass and slag in which crystals are visible without the aid of hydrofluoric acid.

Thus Prechtl melted a considerable quantity of feldspar with one and a half cwt. of glass and cooled the mass in water. In the inside of the lump, where the refrigeration had been more gradual, were found numerous crystals of feldspar, with well defined angles and edges, one of the crystals having the volume of a cubic inch.

Among the specimens of glass with perceptible crystals illustrated by Leydolt are the following:

1. Green flint glass, perfectly transparent, containing opaque grains, which are resolved by the microscope into well defined octahedra of one-half a line in diameter.

2. A glass flux, of emerald color, containing many groups of four-sided prisms, of white tinge and pearly luster.

3. A large mass of blackish green glass, with prismatic crystals singly and in aggregations, also fibrous crystals in globular tufts. The color of the crystals is dirty yellow, passing into green; their luster pearly. They had a rhomboidal section, and were a line in length by one-eighth of a line in thickness.

4. A bluish green English glass, containing tufts of needles uniting to globules of one and a half lines in diameter.

5. A glass flux, of red and green color, containing a large quantity of small four-sided prisms, solitary, and in tufts. The prisms were transparent, and of the same color as the glass, so that they could only be distinguished by the different degree of their refraction and that of the matrix.

6. A vitreous iron slag, of bottle-green color, containing perfect cubes of whitish tinge and pearly luster; also feathery crystals.

7. Another specimen of iron ore slag, similar to the last; but in which the cubes are larger, of nearly the color of the glass, and more equally diffused through the mass.

In a similar slag the cubes were of olive-green color, and in another specimen the cubes were sparse and accompanied by feathery crystals. To these may be added the observations of Splitgerber (Pogg. Ann., lxxvi, 566), that in a lead glass slag presented to Faraday by H. Rose, he found large and well defined six-sided tablets. In a glass prepared with 100 silica, 40 soda, and 10 carbonate of lime, which were perfectly fused and suffered to cool slowly for six hours, he discovered fine acicular crystals grouped star-wise, like flakes of snow. These floated in quantity in the melted liquid, and disappeared when the temperature of the crucible was raised again.

Leydolt's experiments of etching were performed by placing slips of glass in a mixture of fluor spar and oil of vitriol; by exposing glass plates to an atmosphere of hydrofluoric acid vapor; or finally by employing a very dilute solution of this acid contained in leaden vessels.

The following are his results:

1. A thick tablet of fine colorless mirror plate glass, after exposure to the vapor, was covered with colorless rhomboidal crystals. They projected from the plate, were perceptible to the touch, and plainly visible to the naked eye, from the contrast between their lustrous surfaces and the rough etched background.

He obtained similar forms by fluor spar and oil of vitriol, and also by the use of the dilute acid. He infers that they are not quartz, which does not dissolve in hydrofluoric acid, but that they are of similar nature to that of their matrix.

2. A flint glass of bluish color, passing into violet, transparent, and apparently homogeneous, yielded crystals by careful etching. Ordinary window glass gave similar crystals which were of the form of rectangular tablets.

3. A pure transparent English glass (a salt cellar), various vessels of French and Bohemian ware, very thick glass stoppers, glass of various colors, such as white bluish or green, and differently tinted glass fluxes and plates, all yielded similar crystals.

4. Some of the dilute residue of the reaction of sulphuric acid upon fluor spar having been left in a beaker glass, etched the same, with beautiful tufts of fibrous crystals, giving the appearance of some specimens of agate.

Leydolt infers from his experiments that all glass consists of an amorphous mass containing a variable proportion of crystals, and consequently; that not only density and composition, but also the more or less uniform distribution of the crystals, and their nature have a marked influence upon the character and optical behavior of the glass.

He deems the following questions to be of importance.

1. Upon what circumstances depends the formation of the crystals in relation to quantity?

2. What influence have the crystals upon optic phenomena?

3. May not their presence have an influence upon the doubly refracting character which glass acquires by heating and sudden cooling; or by pressure?

4. What substances may be dissolved in melted glass and separated therefrom by slow cooling?

Daubrée (C. R., xlv, 792) obtained various crystals by exposing glass for weeks to the action of water and steam in sealed iron vessels, at a temperature of 400° C. The glass was converted into a white, swollen, kaolin-like substance, composed almost entirely of crystalline particles. He found many crystals of quartz, and also acicular forms of nearly the same composition as Wollastonite (53 p. c. silica, 46 lime; with traces of magnesia). The quantity of water equalled half the weight of the glass, and the action of the water was the same as that of the steam.

Daubrée does not believe that the crystals preëxisted in the glass; but were formed by the action of the water. Although this is probable, it may be questioned whether some of the crystals were not ready formed in the glass.

My own experiments were performed by dropping strong liquid hydrofluoric acid upon plates of glass, using one or successive drops, according to the degree of etching desired. By this means the energy of the acid is expended upon one particular spot of the glass, and by taking more or less of the solvent, or by employing it of greater or less strength, the reaction is completely under control.

The acid was generated in the usual manner in a leaden retort with a condensing tube of the same metal, cooled with a mixture of salt and ice; the liquid acid was received in a platinum crucible, also refrigerated.

The following are the results of the experiments:

When the vapor escaping from the crucible was condensed upon plates of glass, a "ground glass" etching, with in some instances distinct traces of crystallization, resulted.

The following is the action of the liquid acid upon different kinds of glass.

1. Greenish window glass, free from lead. One drop of the acid acted energetically, coating the glass with a white sediment. When washed, the spot was found to be deeply etched, and presented a roughened although transparent appearance. Under the microscope, with oblique, transmitted light, the surface was found to be covered with a web of acicular crystals, crossing at all angles, and presenting exactly the appearance of sublimed caffeine. The average length of the needles was 0·08 of a millimeter; their thickness somewhat less than 0·006 mm.

It was difficult at first to determine whether the crystals were elevated, or depressed below the surface of the plate, in which case they would have represented casts of crystals dissolved out by the acid; but by careful management of the light, studying the shadows and comparing them with caffeine crystals, they were judged to be in relief. Polarized light had no effect upon them. Beside these crystals, there were observed scattered over the field of view a few irregular etchings, in intaglio, which seemed to be casts of crystalline scales dissolved out by the hydrofluoric acid.

2. A piece of the same plate of glass was treated with successive drops of the acid upon the same spot, waiting to add a drop until the reaction of the former one had ceased.

A deep etching was the result, and the extensively corroded surface presented here and there a ground glass appearance. Acicular crystals were apparent, although not as well defined as in the former example.

Nos. 3, 4 and 5 were slips of the same glass etched by vapor. Of these No. 3 was very slightly corroded; upon No. 4 and still more upon No. 5, the action was of greater duration. In these examples the evidence of acicular crystallization was apparent, as a shading upon the ground glass surface. Toward the edges of the etched spot the needles were as distinct as in example No. 1. Here a few well defined prisms with oblique extremities and one or two very small rhombic tablets were observed.

No. 6. Mirror plate glass. This specimen was corroded by a drop of the acid with greater uniformity than the window glass, although the etching was not so deep. It required careful management of the light to detect the crystals which were observed here and there in the form of scales or tablets, apparently broken and very small. A few acicular crystals were also detected.

No. 7. Plate glass (microscope slide). This specimen, when etched, presented the same appearance as No. 6. Very small acicular crystals distributed sparsely over the field of view could be seen.

No. 8. Three specimens of thin glass covers for microscopic objects. The etching of these was very uniform. Numerous and extremely minute needle-shaped crystals, requiring a high power for their definition, were observed.

No. 9. Green bottle glass (two specimens). In these the crystallization was different from that of the former examples. In some places the etching was granular, as if small and short crystals had been removed by the acid. In other places blade-shaped crystals were apparent; these had a tendency to unite in star-like groups, as in snow. Upon one portion of the plate a few small squares and triangles (insoluble in water) were seen.

No. 10. Two specimens of Bohemian glass combustion-tube etched upon the inside. These yielded a granular, very regular etching, and presented a very delicate ground glass appearance, which was resolved by the microscope into small crystalline tablets or scales, apparently fragments of crystals.

No. 11. Bohemian beaker glass; two specimens, of which one was attacked upon the outside, and the other upon the inner surface of the vessel. Small acicular crystals, resembling those of No. 1, but better defined, and a few squares, triangles and trapezoids were detected.

No. 12. Lead glass tubing; two specimens, etched upon the inside. The action of the solvent was energetic. The etching was granular, with numerous short and minute needles, requiring a high power of the microscope for their definition.

No. 13. A portion of a soda glass flask etched upon the inside. This was corroded very readily and yielded plenty of needles resembling in appearance those of No. 1.

No. 14. Lead glass; inside surface of a matrass. The action of the hydrofluoric acid upon this specimen was energetic. The crystals presented the appearance of confused broken tablets, with here and there a needle-shaped crystal.

The acid employed in the experiments gave no etching when dropped upon the different surfaces of a clear transparent quartz crystal.

No. 15. After having completed the preceding series of observations the object-glass of the microscope was protected from the action of the hydrofluoric acid by cementing upon it a plate of thin glass with Canada balsam. A large number of experiments were then made with slips cut from the same piece of window glass, similar to No. 1, with the object of ascertaining by the microscope whether the residue of the reaction was crystalline, and whether, if so, it could have any influence upon the

etching to give an *appearance* of crystals having in reality no existence.

The acid employed was strong enough to hiss when water was added, and emitted copious fumes. Dropped upon the glass it spread, forming a thin circular cake or film of solid substance having a granular appearance.

By a close inspection small prisms or needles were visible here and there in this residue. They were not as numerous as the etched crystals perceptible when the glass was cleansed, and it was not certain that they were not shadows of the glass crystals. In some cases larger prisms could be seen near the edge of the disc; these might be removed by the needle point; but under them was found no corresponding etched appearance of a crystal.

In one instance the slip of glass was coated with wax for the purpose of confining the acid to a small disc where the glass was laid bare. This gave beautiful crystals, similar to the other specimens. When the plate was covered with a thin film of oil the crystalline etching resulted as in the former instances. When the acid was constantly stirred upon the plate with the platinum spoon employed for dropping it, the crystalline etching resulted as before.

No. 16. At length an etching was found which served as an *experimentum crucis* to the question of the protecting action of the residue. In this case the acid was slightly diluted, but still fumed in the air. The glass, after having been acted upon, contained circular white patches of a ground glass appearance. By the microscope these were resolved into groups of star-shaped crystals which, in some cases, were indistinct from corrosion; in others they were plainly crystals. Their appearance was exactly similar to that of the snow-flake, viz., stars composed of needles which were combined with smaller needles forming feathery rays. In two places long needles of one-eighth of an inch in length were visible. Beside these, the acicular web of the former specimens covered the glass. These starry crystals were undoubtedly in *intaglio*. The depression could be distinctly felt with a needle when observing under the microscope, and fine powder of vermilion filled the rays. When first viewed, before the glass was cleansed perfectly, the corroded remains of the crystals could be removed from the depressions with a needle point.

Now while we can conceive that a crystal formed by the action of an acid, might adhere so closely to the glass as to retard the corrosive effect of the acid under it, it is impossible to see how such a crystal could eat away the glass beneath it and thus sink itself under the surface.

In some of the other specimens these starry groups were perceived; but in no case as distinctly as in this one. There happened here to be groups of crystals which were large and very

favorably disposed for the etching process. The result of this series of experiments seemed to throw some doubt upon the "elevated" character of the acicular web of crystals; at least as much doubt as may arise from the difficulty of judging the question from the shadows. The former conclusion was reached by a comparison of the shadows with those of a web of crystals of sublimed caffeine which were known to be in relief. If in intaglio, their depression is too slight to be able to form a judgment by rubbing the etching with vermilion powder. But as the stars are known to be depressions, it may be that the scattered needles are of the same character.

In some examples, two rays of a star-shaped crystal were seen giving the form of a V, which in other cases was transformed into a triangle by an additional needle happening to lie at its base. The Λ shaped crystals described upon a former page may be formed in this manner, although they were not so determined.

It results that the window-glass examined contains crystals already formed, of which some are more soluble in hydrofluoric acid than their matrix and perhaps others less soluble in the same reagent.

All of the specimens of glass submitted to the action of hydrofluoric acid yielded crystalline forms. Those of the window glass are similar in appearance to the crystals obtained by Pelouze by the slow cooling of the same kind of glass after it had been maintained for several hours at incipient fusion. Since in the experiments of this chemist no alteration of weight was observed and the normal character of the glass was restored by simply melting, it is probable that the crystals are of the same nature in both instances. It would appear from some of my observations as if the crystals first formed during the refrigeration of the glass, were subsequently broken by the operations of pressing, rolling &c., to which the material had been subjected.

Doubtless additional interesting phenomena might be observed by a more extended study of different varieties of glass under different conditions by the use of this method.

An analogous action of certain solvents upon other supposed amorphous bodies, as the resins, &c. may demonstrate a crystalline character in them.

From a more extended study of this interesting subject, results the most important respecting the true nature of glass may be expected.

The effect of annealing may here find its true explanation.

If we were able to produce at will an interlacement of long fibrous transparent crystals, a glass of superior flexibility and strength might be obtained. It would also be interesting to ascertain what kind of crystals of different substances might be introduced into glass without destroying its valuable properties.

If such, having the crystalline character of mica or asbestus, could be added a valuable product might result.

Leydolt observed in a slag (see his No. 7) cubic crystals of nearly the same [illegible] the glass and visible to the eye. If we could ascertain the natu[illegible] the glass crystals as well as that of the matrix (which may also be crystalline) [illegible]ly we might, by the laws of isomorphism, be able to colo[illegible] crystals at will, thus producing new and beautiful effects in articles of glass-ware. In this connection Leblanc's observation of protoxid of iron in the transparent portion and but traces of this base in the crystalline part of a specimen of glass, may be noted.

The detection of the crystalline nature of glass demonstrates that we are as yet unacquainted with the true character of this complex substance; but at the same time it indicates the path to be pursued for acquiring this desirable knowledge.